<Organic Materials Chemistry> Organic Structural Chemistry

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- Organic Structural Chemistry -

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Scope of Research

Fundamental studies are being conducted for creation of new functional materials with novel structures and properties. The major subjects are: synthetic and structural studies on novel cyclic π-conjugated systems, particularly the positively charged species stabilized by σ-π interaction; synthesis of new redox-active and supramolecular π-systems; organochemical transformation of fullerene C_{60}, specifically the synthesis of fullerene dimers and trimers by the use of mechanochemical solid-state reactions; synthesis and reactions of open-cage fullerene derivatives; generation of alkylated C_{60} cation and its application for synthesis of functional materials.

Research Activities (Year 2003)

Presentations

Synthesis of Open-Cage Fullerene Derivatives and Encapsulation of Small Molecules, Komatsu K, Murata Y, Murata M, The 203rd Meeting of the Electrochemical Society, 28 April, Paris, France.

Generation and Properties of Functionalized Fullerenyl Cations, Kitagawa T, Lee Y, Murata Y, Cheng F, Komatsu K, 225th ACS National Meeting, 24 March, New Orleans, USA.

Radical Cations and Dications of Oligothiophene Annelated with Rigid σ-Frameworks, Nishinaga T, Komatsu K et al., Gordon Research Conferences on Physical Organic Chemistry, 29 June, Laconia, USA.

Synthesis and Electrolytic Polymerization of a Fullerene-Terthiophene Dyad, Murata Y, Suzuki M, Yamazaki T, Komatsu K, The 203rd Meeting of the Electrochemical Society, 2 May, Paris, France.

Grants

Komatsu K, Appearance of biradical character in π-conjugated hydrocarbons by annelation with strained bicyclic frameworks, Grant-in-Aid for Scientific Research (B) (2), Apr. 2002 - Mar. 2004.

Kitagawa T, Grant-in-Aid for Scientific Research (C) (2), Apr. 2002 - Mar. 2004.

Nishinaga T, Grant-in-Aid for Young Scientists (B), Apr. 2002 - Mar. 2004.

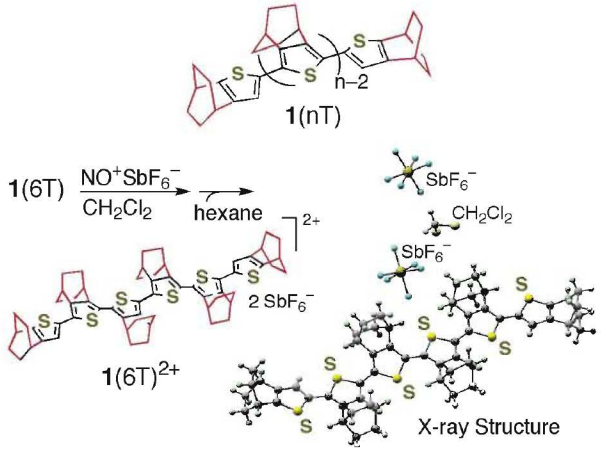
Murata Y, Grant-in-Aid for Young Scientists (B), Apr. 2002 - Mar. 2004.

Kitagawa T, CREST, Japan Science and Technology Corporation, Nov. 2002 - Oct. 2007.

Murata Y, Komatsu K, Academic-Industrial Cooperative Research Fund, Aug. 2002 - Mar. 2004.

Stable Radical Cations and Dications of Oligothiophenes Surrounded by Bicyclo[2.2.2]octene Units

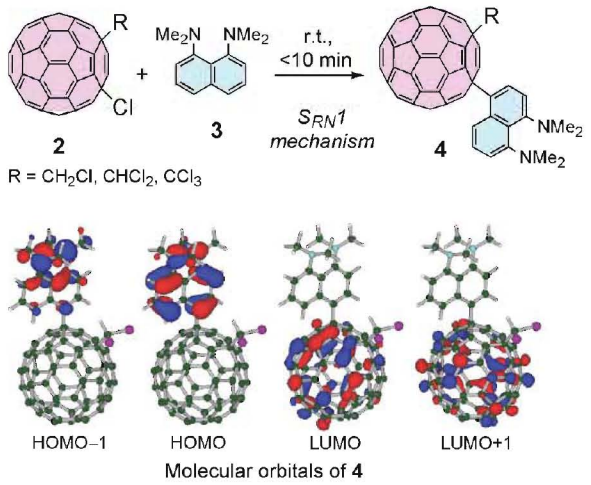
Oligothiophenes **1** annelated with bicyclo[2.2.2]octene (abbreviated as BCO) units were designed and synthesized in order to elucidate the uni-molecular properties of cationic oligothiophenes.[1] The radical cation salts of the dimer and trimer and dication salts of the tetramer and hexamer have been isolated as air-stable single crystals and their structures have been determined by X-ray crystallography. In these crystals, the effective inhibition of intermolecular π-π interaction by BCO units was shown,[2] indicating that **1** is a suitable system for the investigation of the properties of longer oligomer dications, the uni-molecular magnetic properties of which (singlet, triplet, or independent biradicals) are still controversial.



1. Wakamiya A, Yamazaki D, Nishinaga T, Kitagawa T, Komatsu K, *J. Org. Chem.*, **2003**, *68*, 8305.
2. Nishinaga T, Wakamiya A, Yamazaki D, Komatsu K, *J. Am. Chem. Soc.*, **2004**, 126, in press.

Electron-Transfer Induced Substitution of Alkylated C_{60} Chlorides with Proton Sponge

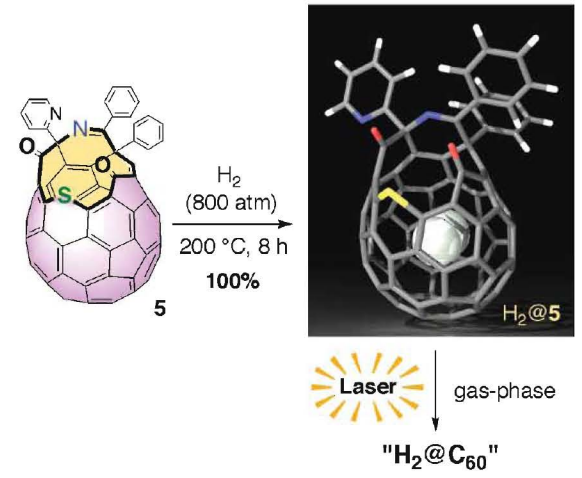
A series of alkylated C_{60} chlorides **2** were found to undergo rapid substitution with proton sponge **3**, affording donor-acceptor dyads **4** in good yields.[3] A chain mechanism, initiated by a single-electron transfer from **3** to **2**, is proposed on the basis of the results of rate measurements. This is the first example of the $S_{RN}1$ reaction observed for alkylated C_{60} chlorides. The facility of such a reaction is reasonably anticipated from the inherent electronegativity of the fullerene core, which was demonstrated by the reduction potential and low LUMO energy of **2**. The present result provides a novel practical method to synthesize fullerene–donor dyads using a variety of electron-rich aromatic compounds.



3. Kitagawa T, Lee Y, Komatsu K, *J. Org. Chem.*, **2004**, *69*, 263.

100% Encapsulation of Molecular Hydrogen in an Open-Cage Fullerene

We succeeded in the synthesis of a fullerene derivative **5** having a 13-membered ring orifice in 40% overall yield based on consumed C_{60} by three-step organic reactions, i.e., a reaction of C_{60} with a 1,2,4-triazine derivative, photochemical oxidation, and insertion of a sulfur atom on the rim of the orifice.[4] A 100% encapsulation of molecular hydrogen in **5** was achieved for the first time by treating solid **5** at 200 °C under 800 atmosphere of hydrogen for 8 hours. Furthermore, when the hydrogen containing molecule, H_2@**5**, was subjected to MALDI-TOF MS at a high laser power, H_2@**5** transformed its structure to H_2@C_{60} by itself in the gas phase. This could be taken as the first step



4. Murata Y, Murata M, Komatsu K, *Chem. Eur. J.*, **2003**, *9*, 1600.
5. Murata Y, Murata M, Komatsu K, *J. Am. Chem. Soc.*, **2003**, *125*, 7152.